<Fundamental Material Properties> Molecular Rheology

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- Molecular Rheology -

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Prof VLASSOPOULOS, Dimitris FORTH and University of Crete, Greek, 20-25 March 2003

Scope of Research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

Research Activities (Year 2003)

Presentations

Tensile Properties of Transparent PC-PDMS Elastomers, Inoue T, ISE2003, 3 April.

Electric Birefringence and Viscoelasticity of Amorphous Polymers, Inoue T, Annual Meeting of the Society of Polymer Science Japan, 15 May.

Electric Birefringence and Viscoelasticity of Amorphous Polymers, Kadoya H, Annual Meeting of the Society of Rheology Japan, 15 May.

Rhology of Carbon Black Systems, Aoki Y, Discussion Meeting of the Society of Rheology Japan, 16 September.

Viscoelasticity of Living Polymers, Oishi Y, Discussion Meeting of the Society of Rheology Japan, 16 September.

Birefringence and Viscoelasticity of Branching Polymers, Matsuno K, Discussion Meeting of the Society of Rheology Japan, 17 September.

Relationship Between Viscoelastic Relaxation Function and Intermediate Scattering Function for Entangled Linear Chain in Early Stages of Tube Dilation Process, Paul A KR, Discussion Meeting of the Society of Rheology Japan, 17 September.

Equilibration of Bridge Population in Block Copolymer Mixed Lamella Systems, Tan H, Discussion Meeting of the Society of Rheology Japan, 17 September.

Rheo-dielectric behavior of poly(ethylene oxide) containing lithium perchlorate, Matsumiya Y, Annual Meeting of the Society of Rheology, 13 October.

Dielectric and viscoelastic behavior of polyisoprene blends: Test of tube dilation mechanism, Watanabe H, Annual Meeting of the Society of Rheology, 14 October.

Electric Birefringence of Amorphous Polymers, Inoue T, Slow Dynamics in Complex Systems, 8 November.

Grant

Paul A KR, Development of a Model for Entanglement Dynamics of Polymers Having Multiple Coarse-graining Scales, Grant-in-Aid for Scientific Research, 1 April 2003 - 31 March 2004.

Award

Kadoya H, Award for the Best Presentation, Electric Birefringence of Amorphous Polymers, The Society of Rheology Japan, 15 May.

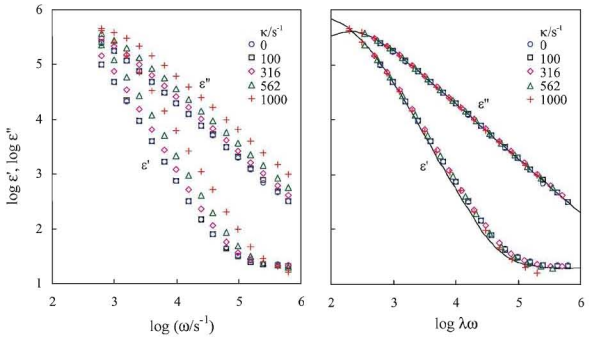
Rheo-dielectric Behavior of Poly(ethylene oxide) Melts Containing Lithium Perchlorate

Electrical properties of polymer electrolyte systems have been extensively investigated. However, many problems remain for the properties under flow. For a model electrolyte, polyethylene oxide (PEO; M = 1000) melt containing lithium perchlorate ($LiClO_4$) at the Li:ethyleneoxide molar ratio of 1:10), we have examined the dielectric behavior at equilibrium as well as under steady shear flow [1].

At the shear rate $\kappa = 0$ (at equilibrium), the PEO/$LiClO_4$ system exhibits significant dielectric dispersion attributable to the electrode polarization of Li^+ ions; see left panel of Figure where the dielectric constant ε' and dielectric loss ε'' are plotted against angular frequency ω. These Li^+ ions form intermolecular bridging of the PEO chains to constrain the chain motion, as evidenced from a significant increase in the zero-shear viscosity η_0 upon addition of $LiClO_4$ to PEO.

Under shear, the ε' and ε'' curves shift to higher ω with increasing κ, and a master curve is obtained when the frequency is normalized with a shift factor λ (< 1); see right panel. These rheo-dielectric features indicate that the flow enhances the ionic mobility μ by the factor of $1/\lambda$ but induces no change in the ion concentration. Indeed, the rheo-dielectric data are well described by the Macdonald theory for the electrode polarization [2] combined with the flow-induced increase of μ; see solid curves in right panel of Figure. Furthermore, the PEO/$LiClO_4$ system exhibited strong shear thinning of the viscosity η with increasing κ and the magnitude of thinning (η/η_0 ratio) coincided with the dielectric shift factor λ. This coincidence reflects a strong motional cooperativity between the PEO chain segment and Li^+ ion.

1. Y. Matsumiya, N. P. Balsara, J. B. Kerr, T. Inoue, and H. Watanabe, *Macromolecules*, **37**, 544 (2004).
2. J. R. Macdonald, *Phys. Rev.*, **92**, 4 (1953).



Rheo-dielectric behavior of PEO/$LiClO_4$ system at 25°C. Solid curves in the right panel indicate the prediction of the Macdonald theory.

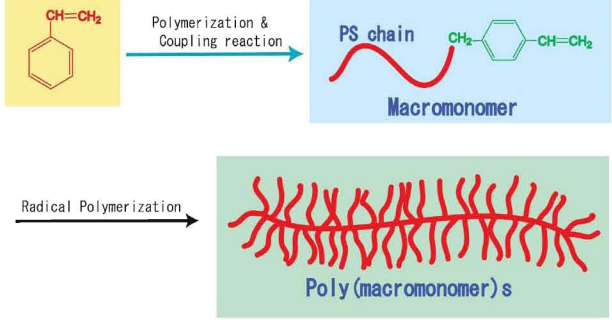
Rheo-Optics of Poly(macromonomer)s

Molecular theories for polymer chain dynamics are based on the concept of statistical segments. For the case of polystyrene, the estimated molecular weight of the segment is approximately 1000, which means one segment conposed of about ten repeating units. Recently, physical properties of new types of polymers having highly branching architecture, like dendrimers and poly(macromonomer)s, have attracted a lot of attention. For such polymers, it is not clear how the concept of the segment should be modified because the distance of the branching points is shorter than the segment size for linear polymers.

When a amorphous polymers is deformed, it becomes anisotropic and birefringent. The strain-induced birefringence reflects the internal stain, and therefore simultaneous measurement of the stress and the birefringence, rheo-optical method, is a useful technique to understand molecular origin of the stress and its relaxation mechanism. [1,2]

Recently, we have synthesized a series of polystyrene poly(macromonomer) and have measured the birefringence and simultaneously the Young's modulus. Comparing with the ordinary linear polystyrenes, we have found that the stress-optical coefficient for poly(macromononer) significantly reduced with increasing of molecular weight of macromonomers (500<M<3000). This result can be attributed to the reduction of the segment size. Thus, we may conclude that the segment size, defined as a unit supporting the entropic stress, is significantly reduced for poly(macromonomer)s. This effect has not been realized untill this study and cannot be well understood from our present knowledge for linear polymers.

1. T. Inoue, H. Okamoto and K. Osaki, *Macromolecules*, **24**, 5670(1991).
2. T. Inoue and K. Osaki, *Macromolecules*, **29**, 1595(1996).



Synthesize of styrene poly(macromonomer)s.